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OF SULFUR DIOXIDE ON CARBON IN AQUEOUS SUSPENSIONS

R. Brodzinsky, S. G. Chang, S. S. Markowitz,  
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KINETICS AND MECHANISM FOR THE CATALYTIC OXIDATION OF SULFUR DIOXIDE  
ON CARBON IN AQUEOUS SUSPENSIONS

R. Brodzinsky,<sup>†</sup> S.G. Chang, S.S. Markowitz,<sup>†</sup> and T. Novakov<sup>\*</sup>

Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

## ABSTRACT

Combustion-produced soot (carbonaceous) particles have been found to be efficient catalysts for  $\text{SO}_2$  oxidation, especially in the presence of liquid water. A kinetic study of the catalytic oxidation of  $\text{SO}_2$  on carbon particles suspended in solution has been carried out. The reaction was found to be first order with respect to the concentration of carbon particles, 0.69<sup>th</sup> order with respect to dissolved oxygen, between zero and second order with respect to  $\text{S(IV)}$  concentrations, and independent of the pH. Temperature studies were carried out, and an activation energy for this reaction was determined. A four-step mechanism is proposed for this carbon-catalyzed oxidation reaction.

## INTRODUCTION

Due to its adsorptive properties, activated carbon has long been used as a scrubber for gases and organic molecules. It is also used as a catalyst in industry for the control of gaseous emissions from smoke stacks. The catalytic oxidation of  $\text{SO}_2$  on activated carbons has been shown to occur (1) and has been used in certain industrial scrubber processes (2). Novakov et al. (3,4) have shown by photoelectron spectroscopy that  $\text{SO}_2$  oxidation can be catalyzed by combustion-generated soot particles and have suggested that this mechanism may be important in the formation of atmospheric sulfates. These studies showed that the soot-catalyzed reaction is more efficient in prehumidified air rather than dry air, but the specific role of water was not clear from their experiments. In the atmosphere, liquid water is important because it may condense on soot particles in stack plumes or in fogs and clouds and affect the chemical processes at the particle surface.

We have examined the effect of liquid water on the carbon-catalyzed  $\text{SO}_2$  oxidation reaction. In this paper, we present a reaction rate law and propose a reaction mechanism for the catalytic oxidation of  $\text{SO}_2$  on carbon particles in an aqueous suspension. (Note: Because in solution  $\text{SO}_2$  can form the three species,  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3^-$  [bisulfite], and  $\text{SO}_3^{2-}$  [sulfite], the terms "sulfurous acid" and " $\text{H}_2\text{SO}_3$ " have been used to signify all the S(IV) species in solution.)

## EXPERIMENTAL

The reaction was studied in systems containing various concentrations of sulfurous acid and suspended carbonaceous particles. The carbonaceous particle concentrations used in the suspensions ranged from 0.002% to 0.32% by weight, and the sulfurous acid concentration ranged from  $7.0 \times 10^{-8}$  M to  $1.00 \times 10^{-3}$  M.

Soots produced by the combustion of acetylene, natural gas, and a diesel engine were collected by impinging the exhaust effluent into water and using this solution as the catalyst by adding sulfurous acid. An activated carbon

(Nuchar-C190, a trademark of West Virginia Pulp and Paper Co.; elemental composition shown in Table I) was used as a model system since it is difficult to prepare reproducible soot suspensions.

Two separate techniques were used to monitor sulfurous acid concentration, depending on the concentration. A Dionex Model 14 anion chromatography system was used for sulfurous acid and sulfate concentrations of less than  $10^{-4}$  M. The operating conditions used were an eluent of 0.002 M NaOH/0.0035 M  $\text{Na}_2\text{CO}_3$  at a flow rate of 138 mL/hr and pressure of 600 psi, through a system consisting of a  $3 \times 50$  mm concentrator,  $3 \times 150$  precolumn,  $3 \times 500$  mm separator, and  $6 \times 250$  mm suppressor columns. Elution times were 10 and 15 minutes for sulfite and sulfate, respectively. For concentrations greater than  $10^{-4}$  M, the concentration of sulfurous acid was monitored, using iodometric titrations during the course of the reaction; and the concentration of sulfuric acid was followed by the turbidimetric method in selected runs.

The pH of the solution was adjusted by the addition of  $\text{H}_2\text{SO}_4$  to  $\text{SO}_2 \cdot \text{H}_2\text{O}$  for  $\text{pH} < 2.5$ , and various combinations of  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{NaHSO}_3$ ,  $\text{Na}_2\text{SO}_3$ , and  $\text{NH}_4\text{OH}$  were used to control the pH above 2.5. The pH was measured using a Beckman digital pH meter with combination probe.

Oxygen-dependence studies were performed in a contained atmosphere glove box with various mixtures of  $\text{N}_2$  and  $\text{O}_2$ . All solutions were allowed to equilibrate prior to the start of the reaction. Dissolved oxygen was measured using a Yellow Springs Instrument Model 57 dissolved oxygen meter.

## RESULTS

Figure 1 shows the typical reaction curves of the oxidation of  $\text{H}_2\text{SO}_3$  in aqueous suspensions of soot particles collected from acetylene and natural gas flames. The reaction occurs in two steps. The initial disappearance of  $\text{H}_2\text{SO}_3$  is so fast that its rate could not be followed by the analytical techniques used.

The second step is characterized by a much slower reduction of  $\text{H}_2\text{SO}_3$ . The results obtained with these combustion-produced soots were reproduced (Fig. 2) by suspensions of similar concentrations of Nuchar-C190. Figure 2 also shows that there is a mass balance between the sulfurous acid consumed and the sulfuric acid produced. Figure 3 shows the effect of varying activated carbon concentration on the reaction. At a constant temperature, the amount of  $\text{H}_2\text{SO}_3$  oxidized by the rapid first step process was found to be proportional to the carbon particle concentration. The rate of the slower process is also proportional to the carbon concentration, which shows a first order reaction dependence.

Figure 4 illustrates the effect of dissolved oxygen concentration on the rate of reaction. The temperature dependence of the rate of reaction is shown in Fig. 5. The rate of diffusion of oxygen into solution does not affect the reaction rate, since the concentration of dissolved oxygen was constant during the course of the reaction. The temperature-dependence data of Fig. 5 were done at pH 2.9. Identical results were obtained at pH 1.2 and 7.0. The oxygen dependence of the reaction is of 0.69<sup>th</sup> order, while the temperature dependence yields an activation energy of 49.0 kJ/mole for the reaction.

The effects of pH are shown for the higher  $\text{H}_2\text{SO}_3$  concentration experiments in Fig. 6. The pH of the solution decreased during the course of the reaction. The change in pH varied from 0.05 to 1.5 pH units, depending on the initial pH of the solution: the larger the initial pH, the larger the change. Our results demonstrate that the reaction rate does not depend on the pH of the aqueous suspension when the pH is less than 7.6. The pH range of our experiments (1.20 to 7.5) covers the range of atmospheric liquid water (rain, fog, etc.). For the activated carbon that was studied, no reaction occurs when the pH is greater than 7.6.

Figure 7 shows the effective rate of reaction (normalized carbon concentration,

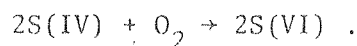
room temperature -- 20°C, and air) as a function of the sulfurous acid concentration. The data points are the instantaneous rates based on three-point averages from the various experiments. The rate of reaction is second order with respect to  $\text{H}_2\text{SO}_3$  below  $10^{-7}$  M, moves through a first order reaction around  $5 \times 10^{-6}$  M, and becomes independent of  $\text{H}_2\text{SO}_3$  concentrations above  $10^{-4}$  M.

In summary, the reaction occurs in two steps -- an initial rapid oxidation followed by a much slower one. The rate of the first step is too fast to follow. The reaction of the second step has the following characteristics:

1. The reaction rate is first order and 0.69<sup>th</sup> order with respect to the concentration of carbon and dissolved oxygen respectively.
2. The reaction rate is effectively pH independent ( $\text{pH} < 7.6$ ).
3. The activation energy of the reaction is 49.0 kJ/mole.
4. There is a balance between the consumption of sulfurous acid and the production of sulfuric acid.
5. The reaction rate has a complex dependence on the concentration of  $\text{H}_2\text{SO}_3$ , ranging between a second and zeroth order reaction as the  $\text{H}_2\text{SO}_3$  concentration increases.

#### DISCUSSION

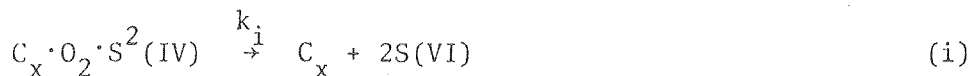
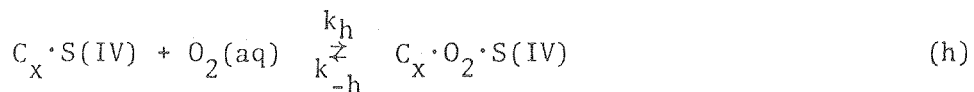
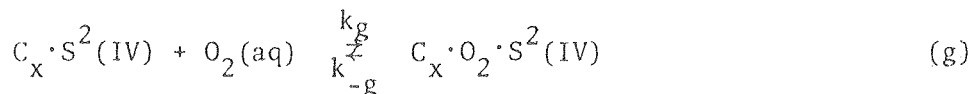
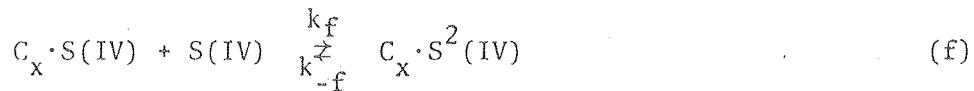
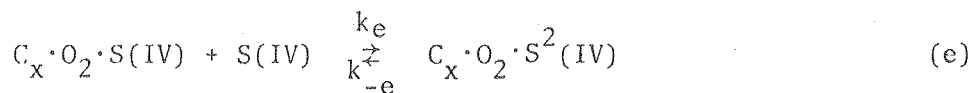
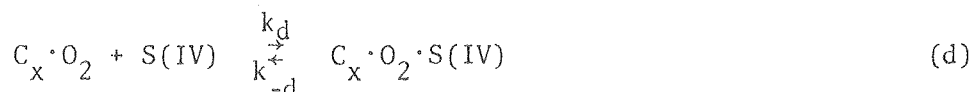
The oxidation of S(IV) to S(VI) can be expressed simply by the symbolic net reaction [Let  $\text{C}_x$  = carbon surface;  $\text{S(IV)} = \text{H}_2\text{O} \cdot \text{SO}_2$ ,  $\text{HSO}_3^-$ , and  $\text{SO}_3^{2-}$ ;  $\text{S(VI)} = \text{H}_2\text{SO}_4$ ,  $\text{HSO}_4^-$ , and  $\text{SO}_4^{2-}$ .]:



The first order reaction rate with respect to the activated carbon catalyst is representative of a surface catalysis. The reaction will proceed via the adsorption of the reacting species onto the catalytically active site. A series of adsorption steps can explain the fractional and varying order of



reaction with respect to S(IV) and O<sub>2</sub>.



Steps a through h are adsorptions on the surface, with the oxidation step occurring in reaction i. Under normal conditions this oxidation is irreversible (as written); and since the reaction does occur in water, the desorption of the bisulfate or sulfate ions can be considered in one step and irreversible.

The rate of production of the sulfate species is therefore

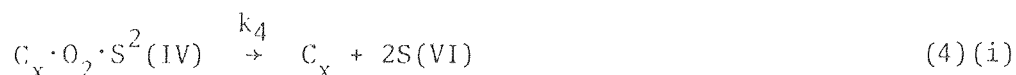
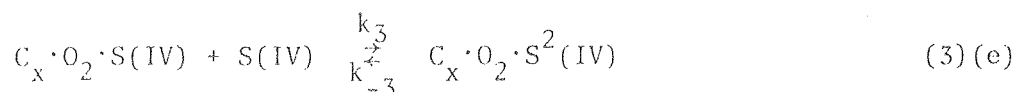
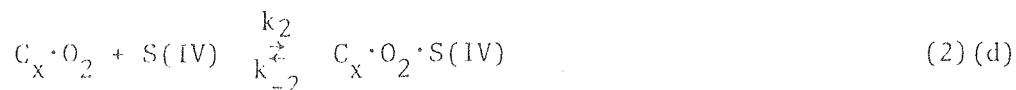
$$\text{Rate} = \frac{d[S(VI)]}{dt} = 2k_i [C_x \cdot O_2 \cdot S^2(IV)] .$$

Steps a and b would both be initiation steps while step c would be an interference as water molecules adsorb onto the active site. A rate expression could be derived with the possibility of two distinct reaction initiators.

The experimentally observed activation energy is similar to the activation energies for the chemisorption of oxygen onto activated carbons as seen by Puri et al. (5). Many reactions have activation energies of this magnitude (50 kJ/mole); however, this agreement, together with the rapid initial oxidation (when the carbon is added to a solution containing  $\text{H}_2\text{SO}_3$ ) indicates that the first

step in the reaction is the adsorption of oxygen onto the active sites. Since the oxygen from the air has already adsorbed onto the carbon prior to going into solution, the rapid initial oxidation would be the reaction of S(IV) species with the already formed  $\text{C}_x \cdot \text{O}_2$  complex. Changing the amount of adsorbed oxygen present changes the magnitude of the initial oxidation. Degassing in vacuum and saturation with nitrogen yields no rapid oxidation; further, as the oxygen concentration increases in oxygen/nitrogen mixtures, so does the magnitude of the rapid oxidation.

Assuming then that the first step in the reaction is the adsorption of oxygen, we have the following four-step reaction:



With the Langmuir adsorption equation,  $[\text{C}_x \cdot \text{O}_2 \cdot \text{S(IV)}^2]$  can be solved for as

$$[\text{C}_x \cdot \text{O}_2 \cdot \text{S}^2(\text{IV})] = \left( \frac{k_3 [\text{S(IV)}]}{1 + k_3 [\text{S(IV)}]} \right) [\text{C}_x \cdot \text{O}_2 \cdot \text{S(IV)}] .$$

For steps 1 and 2, the following is derived in a similar manner for the rate

expression:

$$\frac{d[S(VI)]}{dt} = 2k_4[C_x] \left( \frac{K_1[O_2]}{1 + K_1[O_2]} \right) \left( \frac{K_2[S(IV)]}{1 + K_2[S(IV)]} \right) \left( \frac{K_3[S(IV)]}{1 + K_3[S(IV)]} \right) \quad (I)$$

where  $K_1 = k_1/k_{-1}$ ,  $K_2 = k_2/k_{-2}$ ,  $K_3 = k_3/k_{-3}$ .

The experimental results yield the following rate law for this reaction

$$\frac{d[S(VI)]}{dt} = k[C_x][O_2]^{0.69} \left( \frac{\alpha[S(IV)]^2}{1 + \beta[S(IV)] + \alpha[S(IV)]^2} \right) \quad (II)$$

where  $k = 1.69 \times 10^{-5}$  moles<sup>.31</sup>·L<sup>.69</sup>/g·sec,

$\alpha = 1.50 \times 10^{12}$  L<sup>2</sup>/mole<sup>2</sup>,

$\beta = 3.06 \times 10^6$  L/mole,

$[C_x]$  = grams of Nuchar-C190/L,

$[O_2]$  = moles of dissolved oxygen/L, and

$[S(IV)]$  = total moles of S(IV)/L.

From the Arrhenius equation, the rate constant may be expressed as

$$k = Ae^{-E_a/RT}$$

where  $E_a = 49.0$  kJ/mole, and

$$A = 9.04 \times 10^3 \text{ moles}^{.31} \cdot \text{L}^{.69} / \text{g} \cdot \text{sec}.$$

Equation I can be changed simply to Equation II. A fractional order adsorption reaction is achieved by substituting the Freundlich isotherm  $\theta = k[X]^n$ , where  $\theta$  is the fraction of the surface covered by adsorbed species X, for the Langmuir (6)  $\theta = K[X]/(1 + K[X])$ .

Multiplication of the S(IV) terms yields the experimentally seen expression, where  $K_2 K_3 = \alpha$  and  $K_2 + K_3 = \beta$ .

Preliminary experiments with other activated carbons, as well as laboratory-generated combustion soots, have shown the same rate law behavior, while the actual numerical constants are different.

The behavior of the reaction with respect to the pH of the solution indicates that all three S(IV) species,  $\text{H}_2\text{O} \cdot \text{SO}_2$ ,  $\text{HSO}_3^-$ , and  $\text{SO}_3^{2-}$ , react in a similar manner; hence our treatment of all species as one in the derivation of the rate law and mechanism. Below a pH of 7.6, the reaction rate is independent of the pH; but when the pH becomes greater than 7.6, the rate abruptly drops to zero. This abrupt drop in the reaction rate above a pH of 7.6 would seem to indicate a poisoning of the catalytically active surface. It has been proposed (7) that the reacting species was bisulfite, but our results differ and indicate that it is the active site that is affected by the pH. Figure 8 shows the behavior of the reaction as the pH is changed rapidly from acid to base by addition of a few drops of concentrated NaOH or  $\text{H}_2\text{SO}_4$ . (Concentrations have been normalized to account for dilution factors). When the activated carbon is placed into a mildly basic sulfite solution, no reaction occurs. When the solution is made mildly acidic, the reaction begins with the expected rate. Similar behavior is seen as the solution is changed back to basic and again to acidic. Studies are planned to examine the behavior of other activated carbons. The catalytic activity may be dependent on the method of activation for the different carbons.

We have done comparisons of this reaction with the rates of the other atmospherically important  $\text{SO}_2$  oxidation reactions (8). As it has been recently shown<sup>9</sup> that carbonaceous particles are a significant portion of the ambient particulate burden, the carbon-catalyzed reaction can be a major contributor to the formation of aerosol sulfates.

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- † Also Department of Chemistry, University of California, Berkeley, CA 94720.

## ACKNOWLEDGMENT

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Table I. Elemental composition of Nuchar-C190 (% by weight).

C	74.7	K	0.091	Ni	0.001
O	23.6	Al	> 0.055	Cl	< 0.001
H	0.9	Ti	0.016	As	0.0004
N	0.1	Mn	0.013	Br	0.0004
Ca	0.221	Cr	0.002	Rb	0.0004
S	> 0.166	Cu	0.002	Zr	0.0004
Si	> 0.111	Zn	0.002	Pb	0.0004
Fe	0.117	Sr	0.002	Ga	0.0001

BET surface area = 550 m<sup>2</sup>/g.

C, H, N: combustion; O: difference; other elements: X-ray fluorescence.

## FIGURE CAPTIONS

Figure 1.  $\text{H}_2\text{SO}_3$  concentration as a function of time for acetylene and natural gas soot suspensions.

Figure 2.  $\text{H}_2\text{SO}_3$  and  $\text{SO}_4^{2-}$  concentrations as a function of time for a 0.16% by weight activated carbon suspension.

Figure 3.  $\text{H}_2\text{SO}_3$  concentration as a function of time for various concentrations of activated carbon suspensions.

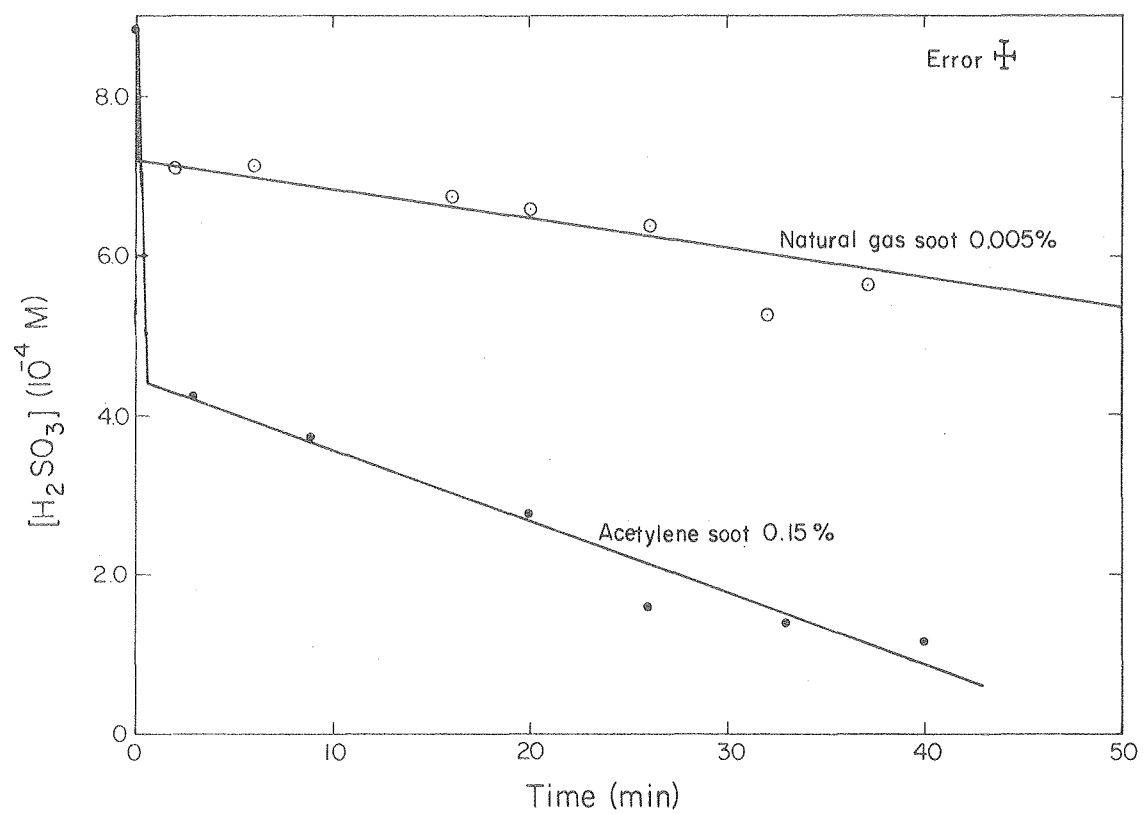
Figure 4. The rate of formation of sulfate versus dissolved oxygen concentration for 0.16% by weight activated carbon suspensions.

Figure 5. Rate constant versus  $1/T$  at  $\text{pH} = 2.9$ .  $E_a = 49.0$  kJ/mole (11.7 kcal/mole).

Figure 6.  $\text{H}_2\text{SO}_3$  concentration as a function of time at an activated carbon concentration of 0.16% by weight at various pH values. Initial  $\text{H}_2\text{SO}_3$  concentration was  $8.85 \times 10^{-4}$  M.

Figure 7. Effective rate of reaction vs.  $\text{H}_2\text{SO}_3$  concentration. Curve is least squares fit to proposed rate expression.

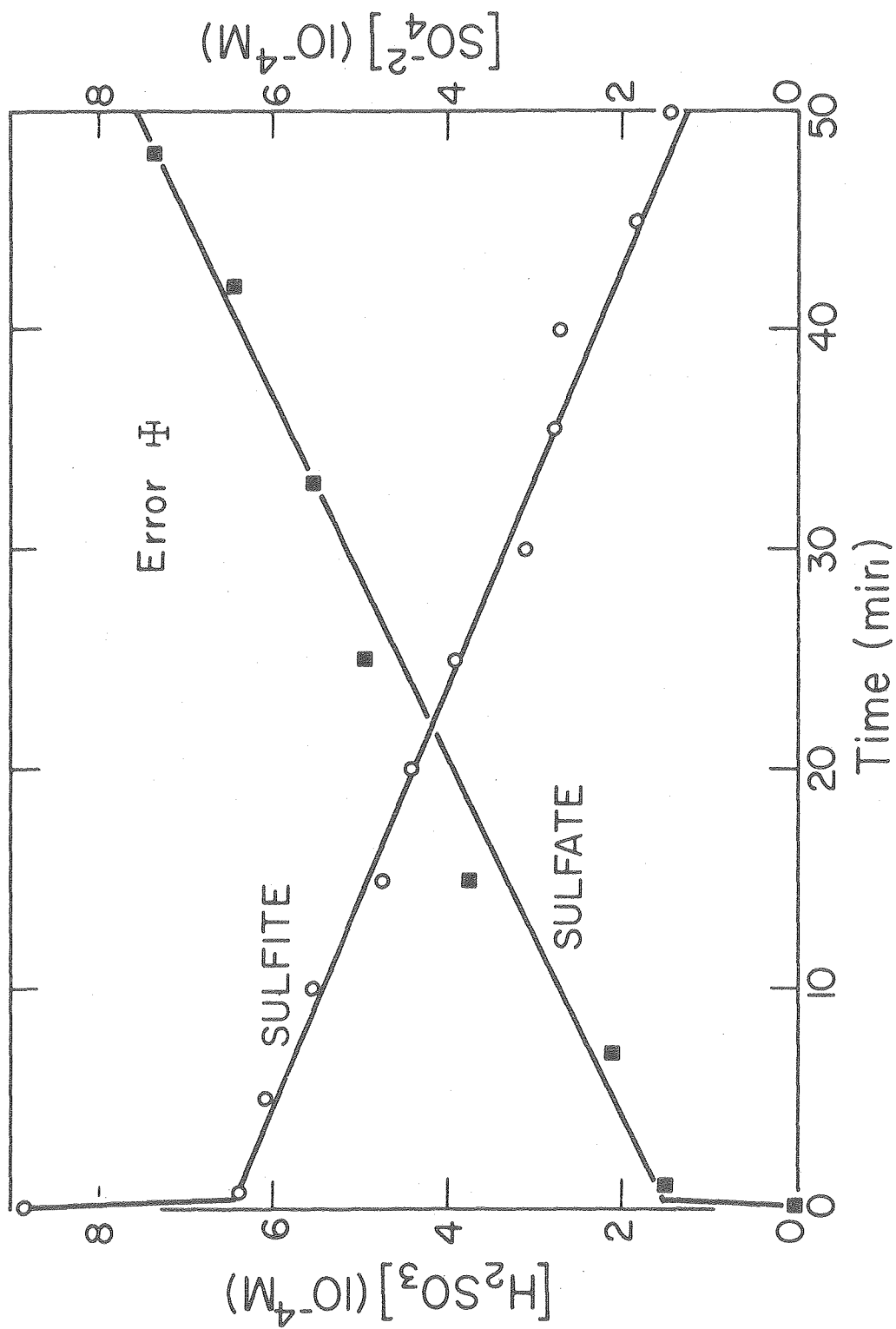
Figure 8. Behavior of  $\text{H}_2\text{SO}_3$  concentration as function of time as pH is quickly changed from base to acid.



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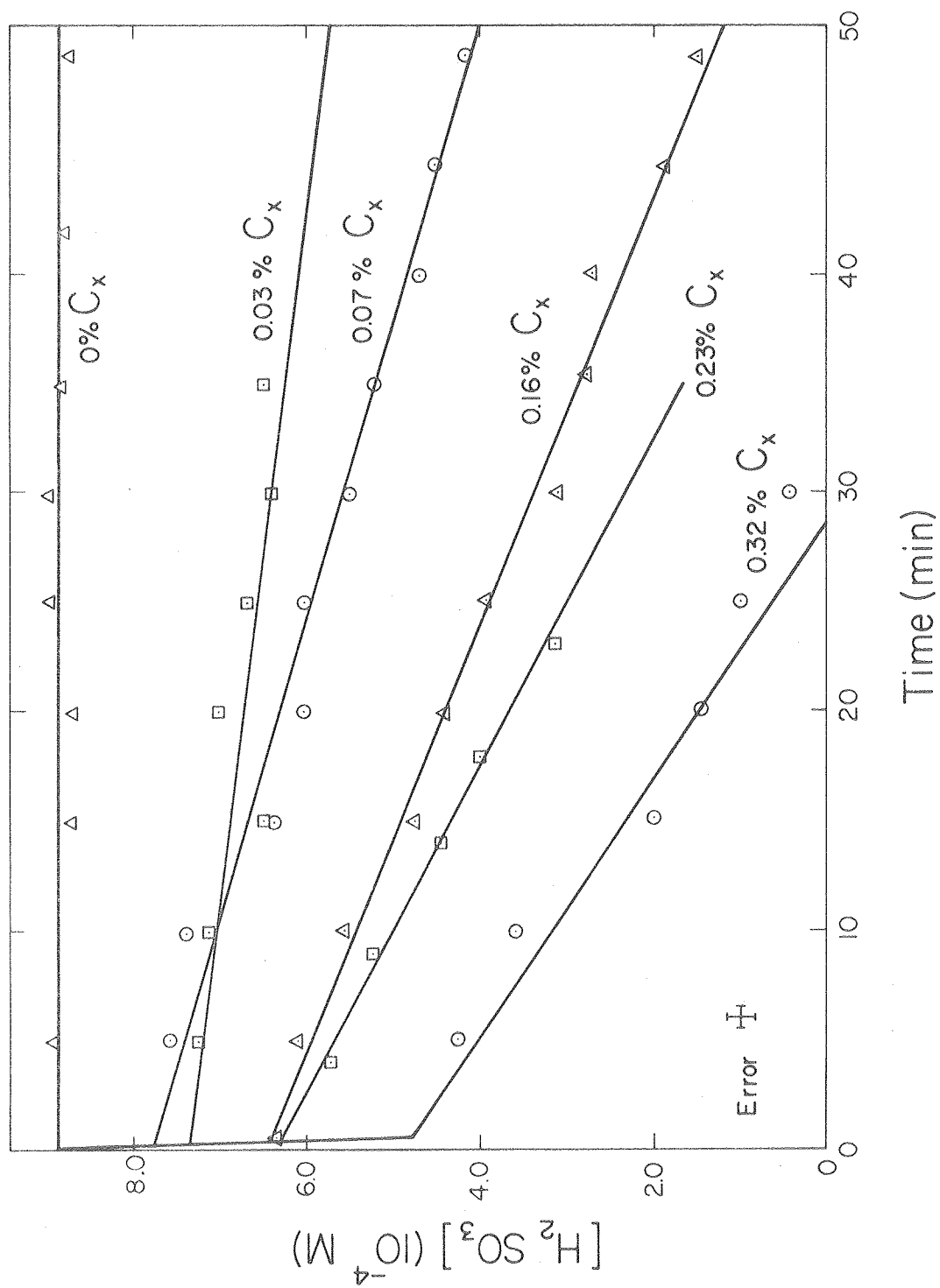
Figure 1





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Figure 2



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Figure 3

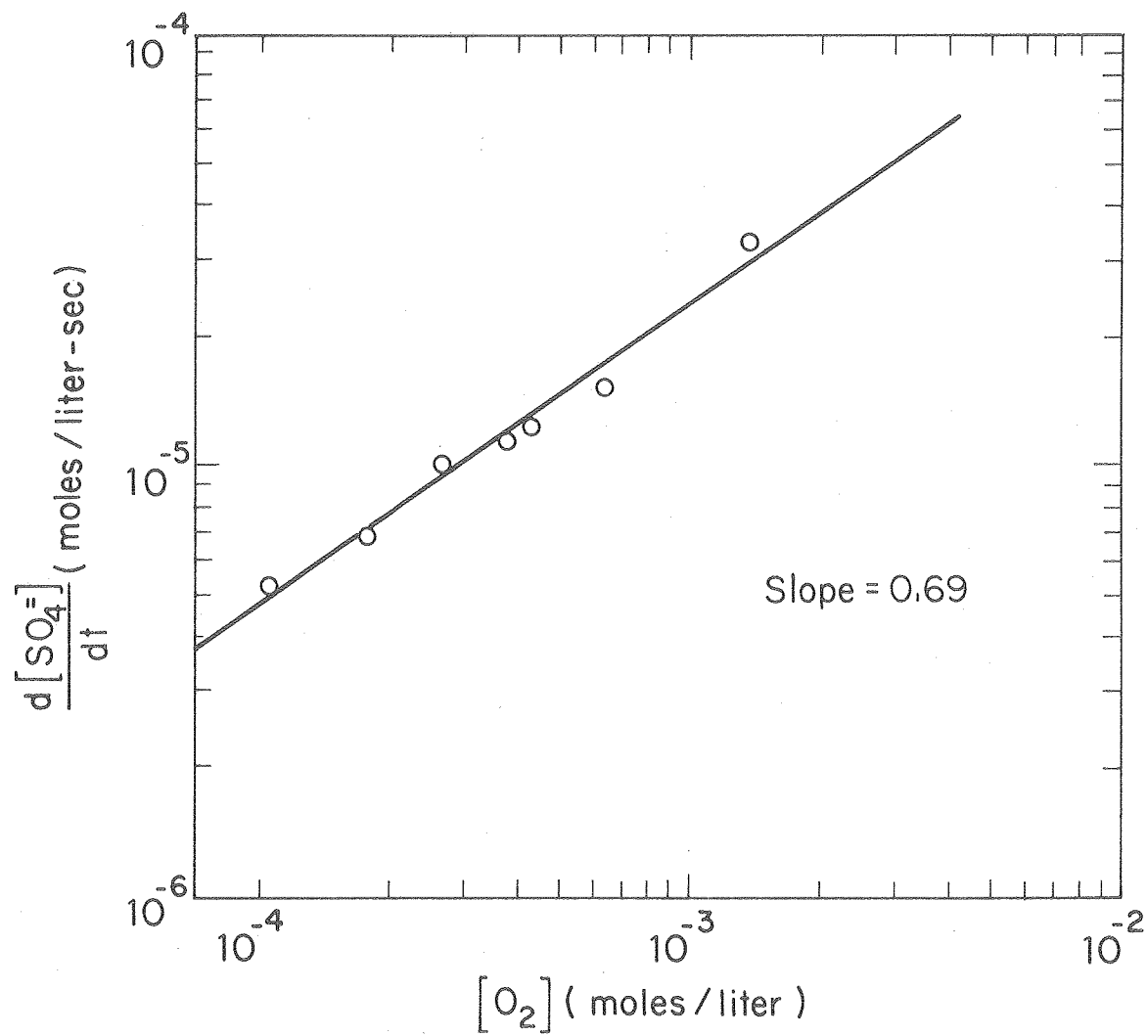
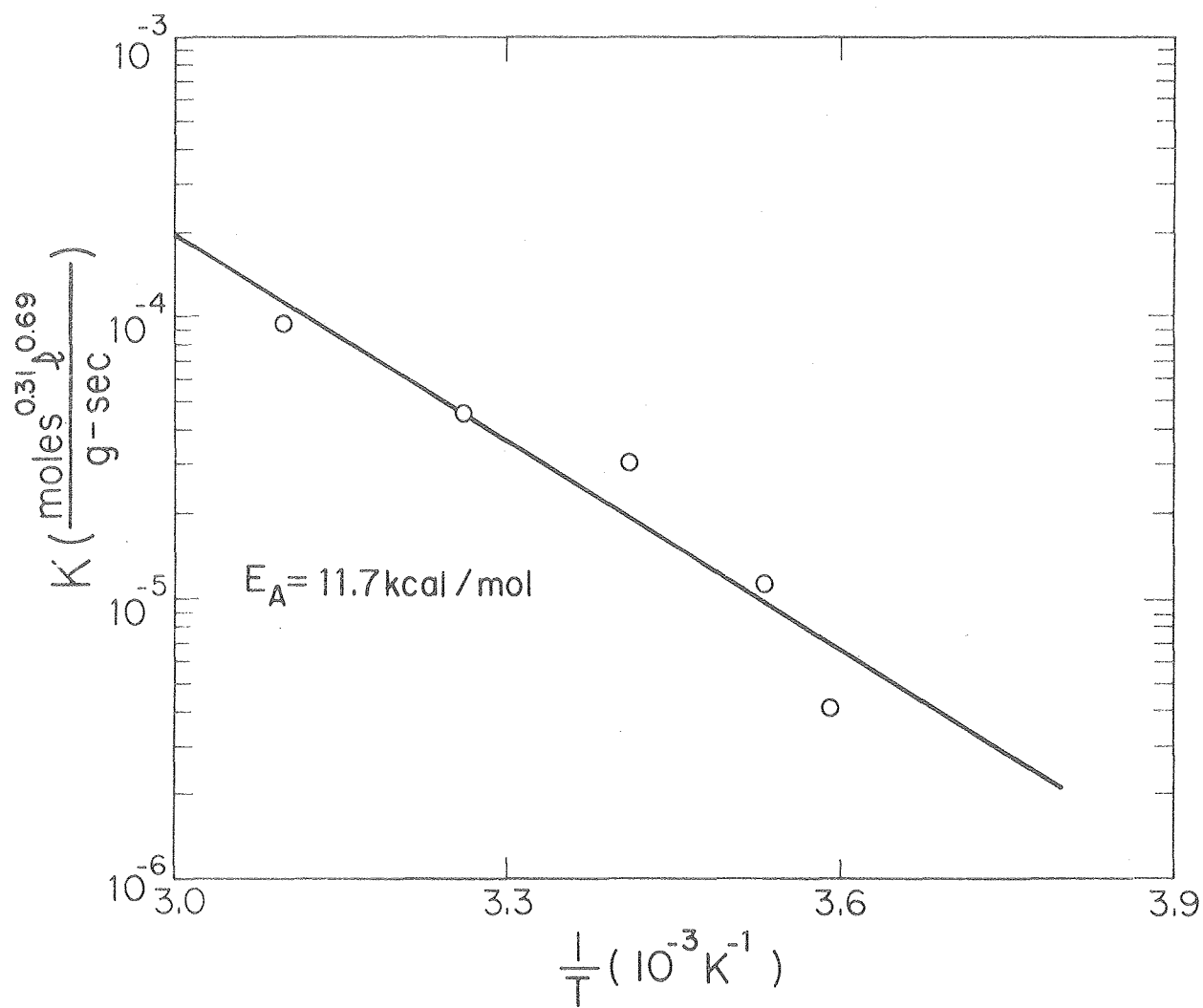


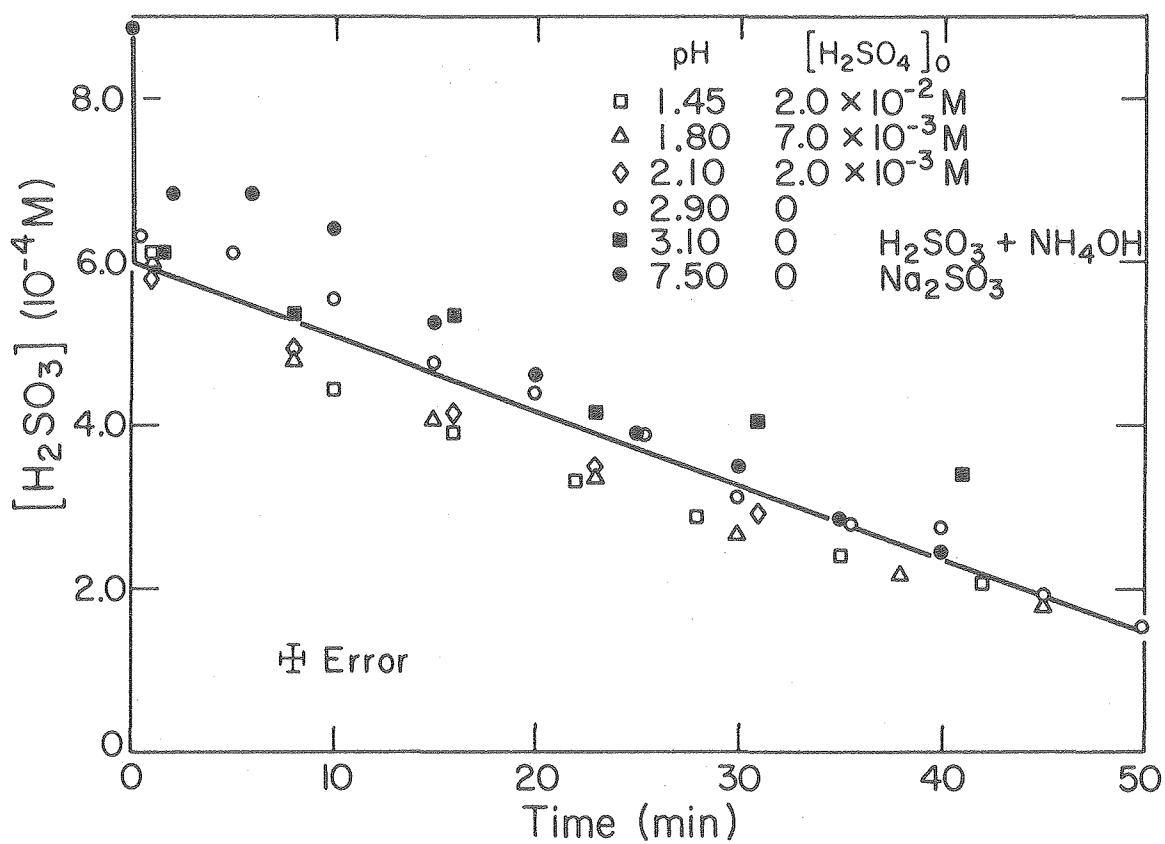
Figure 4

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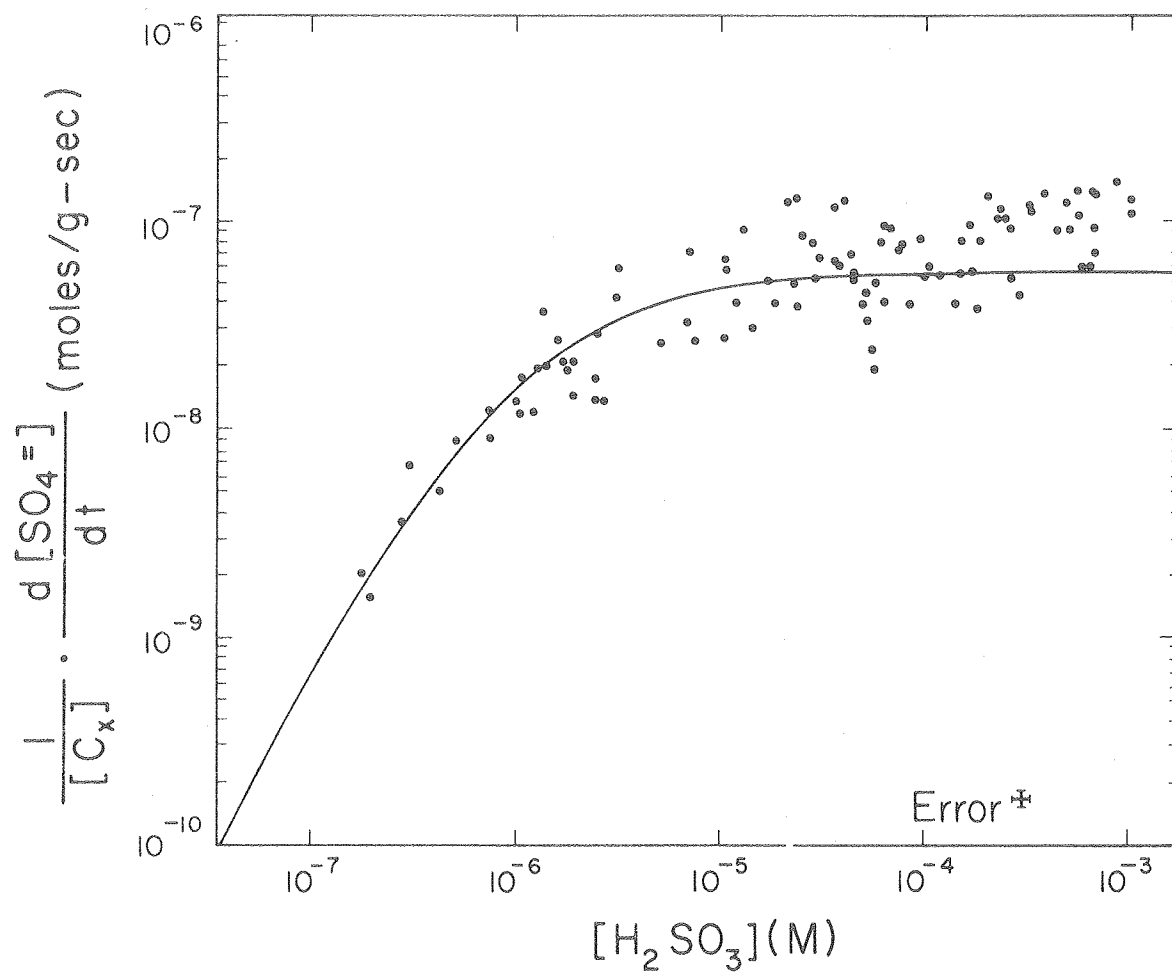
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Figure 5



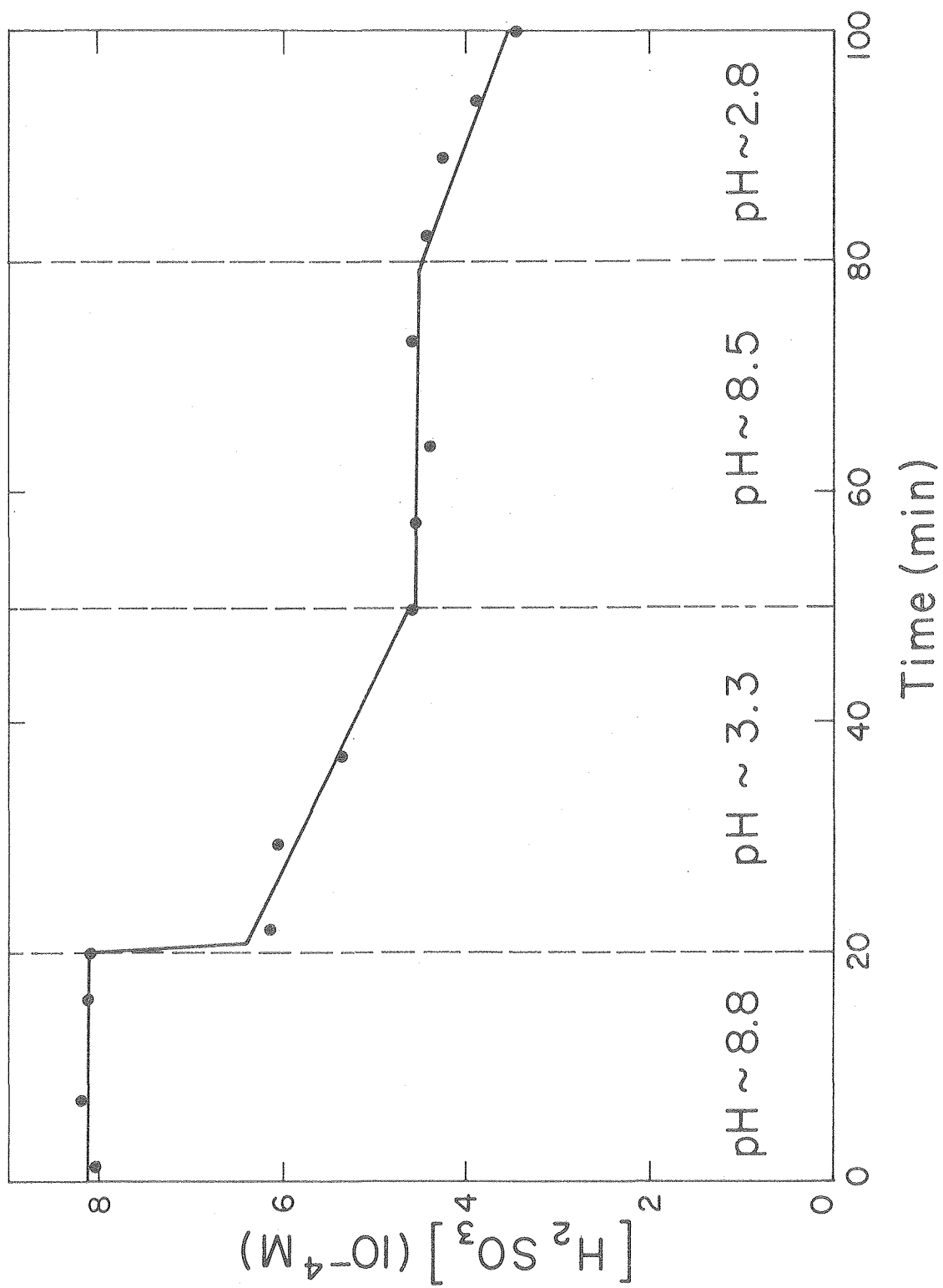
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Figure 6



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Figure 7



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Figure 8

